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EXECUTIVE SUMMARY

ASSESSMENT OF MIXED-BED IX CAPACITY FOR CAN-DECON SERVICE

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Calculations based on design conditions and the manufacturer's resin capacity data indicated that both the anion and cation exchange capacities of the CAN-DECON mixed-bed ion exchange column at Bruce NGS would be very marginal in meeting the requirements of the August 29, 1986 decontamination. According to the calculations, the total exchange capacity contained in the 160 ft^3 (4.53 m^3) of mixed-bed Amberlite IRN 150 resin with an anion resin enrichment of 50 ft^3 (1.42 m^3) of IRN 78 resin would be adequate for processing the design volume of 300 m^3 of solution only under the ideal conditions (ie, the solution composition exactly corresponds to the design conditions, no ionic impurities are present in the solution, and the IX resin utilization is 100%). For practical purposes the column capacity would be insufficient (eg. assuming 80% operating efficiency or a solution containing some oxalate precipitates or other cations such as ferric, manganese, nickel etc.).

However, the experimentally determined 'operating capacity' was much higher than that calculated. One possible explanation for this discrepancy is that the reagent anions and metal cations in solution, when mixed, tend to form complex anions and complex cations which tend to reduce the respective exchange capacity requirements. Additional experiments and computer simulation of the equilibrium distribution of the complex ions were carried out to assess the plausibility of this explanation. The experimental results agreed qualitatively with the predictions of the computer program CANDMAN /1/. Quantitative agreements are difficult because the computer model simulates the limiting equilibrium conditions in the feed solution, which cannot be maintained in the column internals.

To obtain a reliable assessment of the column capacity, it is recommended that for each set of design conditions two estimates be made, one based on experimental results, and the other based on computer simulations; and that the more conservative estimate be selected. For the case of Bruce NGS CAN-

DECON, the mixed-bed column is estimated to be capable of processing 410 m^3 of the design-condition solution, which is in excess of the design requirement of 300 m^3. Or alternatively, after processing the design volume of 300 m^3, the column should have sufficient residual capacity to remove up to 40 kg of ferrous oxalate (resulting from precipitation of iron with 25 kg of oxalic acid $C_2H_2O_4$ or 35 kg of $C_2H_2O_4.2H_2O$, which was being considered for addition to the system to form the ferrous oxalate expected to function as a corrosion inhibitor).

This work has also illustrated that design calculations for IX columns in CAN-DECON service cannot be based on manufacturer's resin capacity data. Owing to the formation of complex ions in CAN-DECON solution, only the operating capacities determined experimentally are reliable. Computer simulation results from the CANDMAN program was found to be useful for the qualitative interpretation of the experimental findings and for verifying that the estimates are sufficiently conservative.

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ASSESSMENT OF MIXED-BED IX CAPACITY IN CAN-DECON SERVICE

F. H. CHANG

In preparation for the Bruce NGS Unit 1 CAN-DECON of August 29, 1986 the mixed-bed ion exchange column was assessed for adequate operating capacity. Estimates based on manufacturer's resin capacity data showed the column capacity to be inadequate, but laboratory experiments indicated the contrary. Additional experiments and computer simulation work were carried out to determine the cause of the discrepancy. In conclusion, the mixed-bed column under consideration should be adequate for processing 410 m^3 of the CAN-DECON solution at design concentrations, which is in excess of the process requirement of 300 m^3. Or alternatively, if the operation limits the solution volume to 300 m^3, the IX column should then have reserve capacity available for removing any ferrous oxalate precipitate formed by addition of extra amounts of oxalic acid. The amount of ferrous oxalate that can be removed is estimated to be 40 kg, which corresponds to an oxalic acid addition of 35 kg (as $C_2H_2O_4.2H_2O$). A second conclusion derived from this work is that design calculations for IX columns in CAN-DECON service cannot be based on manufacturer's resin capacity data. Owing to the formation of complex ions in CAN-DECON solution/1/, only the operating capacities determined experimentally are reliable. The effects of complex ion formation on the resin exchange capacity have been explained with the aid of the computer simulation results obtained from the CANDMAN program/1/.

1.0 INTRODUCTION

The Bruce NGS CAN-DECON mixed-bed IX column is designed for loading with 160 ft^3 (4.53 m^3) of mixed-bed resin (Amberlite IRN 150) enriched by 50 ft^3 (1.42 m^3) of anion resin (IRN 78). The design basis is given in Table 1.

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TABLE 1

DESIGN BASIS FOR BRUCE
CAN-DECON MIXED-BED IX COLUMN

COLUMN

COLUMN I.D. = 1.98 m (6 ft 6 in)
COLUMN HEIGHT = 2.74 m (9 ft)
SOLUTION FLOWRATE = 42 kg/s
VOLUME OF SOLUTION = 300 m^3
OPERATING TEMPERATURE = 35 - 60°C

SOLUTION

		CONCENTRATION (ppm)	IONS IN 300 m^3 SOLUTION (g-eq)
ANIONS	EDTA	500	2055
	OXALIC	80	533
	CITRIC	200	938
	Total =		3526
CATIONS	Fe^{2+}	200	2150
	Total =		2150

RESINS

		RESIN CAPACITY (meq/mL)	RESIN VOLUME (L)	CAPACITIES IN 210ft^3 RESIN (g-eq)
ANIONS	IRN 150	0.55	4531 (160 ft^3)	2492
	IRN 78	1.10	1416 (50 ft^3)	1558
	Total =			4050
	80% Eff. =			3240
CATIONS	IRN 150	0.55	4531 (160 ft^3)	2492
	Total =			2492
	80% Eff. =			1990

Preliminary calculations by CNS revealed that the column capacity might be inadequate for the required service. The lack of capacity would also limit the ability of adding any extra amounts of oxalic acid to the system to form ferrous oxalate as a corrosion inhibitor, since the extra amounts of oxalate must be removed at the end of the decontamination. This work was then initiated to study the situation in greater depth, and assess the capacities more realistically.

According to the manufacturer's data, IRN 150 has an exchange capacity of 0.55 meq/mL of resin for both anion and cation exchange, and IRN 78 has 1.1 meq/ml of resin for anion exchange. The total maximum capacity of the column would then be 4050 g-eq for anion exchange and 2492 g-eq for cation exchange. These capacities would be marginally sufficient to process the design volume of the solution (300 m^3) with no provision for removal of additional oxalate. As indicated in Table 1, when an operating efficiency or safety factor of 80% is incorporated, the resultant capacity values would be less than that required by the service. The cationic capacity could also be judged inadequate if one assumes a certain proportion of trivalent iron (Fe^{3+}) in the solution, or if other metals were present. For practical purposes, therefore, the calculated capacities could be considered inadequate.

Yet, in the attempt to verify the estimates experimentally by determining the operating capacities in laboratory column runs, it was discovered that the capacities were more than adequate. Additional experiments were then undertaken and theoretical computer simulations were carried out to address the discrepancies.

2.0 EXPERIMENTAL

The experimental conditions of the seven test runs are summarized in Table 2. Run 1 used a large Plexiglas column (height = 4 ft or 122 cm; ID = 1 inch, or 2.54 cm), and the experiment was conducted at room temperature of about 22°C due to the lack of large heating facilities. The column sizes of the remaining six runs (Runs 2 to 7) were compromised (column ID = 1.5 cm, height = 36 cm) to permit experiments at the elevated design temperature of 35°C. The flowrates were adjusted to result in residence times comparable to those of the actual operation at around 2.4 minutes.

The apparatus consisted of standard glass IX columns loaded with ion exchange resins IRN 150 and IRN 78 mixed according to design conditions; glass and plastic containers were used for the stock solution. The feed stock solution was prepared in a 2.5-litre Pyrex reservoir, by circulating solutions containing predissolved EDTA, oxalic acid and citric acid reagents through a glass column containing steel wool until the required level of metal ion concentration was reached. The concentration of the metal ion was monitored by on-the-spot atomic absorption analysis.

As shown in Table 2, the concentration of oxalic acid in the feed solution of the two initial runs, Runs 1 and 2, was very low. This was due to the difficulties encountered in the initial attempts to dissolve steel wool and reagent solids (including oxalic acid) simultaneously in glass flasks. The chemical composition was better controlled in all subsequent runs, with the

TABLE 2

SUMMARY OF EXPERIMENTAL CONDITIONS

Run No	Operating Parameters						Solution Concentrations (ppm)					
							Reagents			Metal Ions		
	Column Dia (cm)	Volume of Resin (mL)	Flowrate (mL/min)	Residence Time (min)	Temp (^{o}C)	Feed Solution pH	EDTA	Citric	Oxalic	Fe^{2+}	Fe^{3+}	Total Fe
1	2.54	690	261	2.36	22	3.9	417	167	17	114	76	190
2	1.5	64	31	2.03	35	3.3	407	169	0	124	76	200
3	1.5	64	28	2.23	35	3.4	473	210	80	173	67	240
4	1.5	64	29	2.21	35	2.6	413	197	74	58	43	101
5	1.5	64	27	2.34	35	2.8	437	207	70	83	44	127
6	1.5	64	28	2.28	35	2.6	409	190	69	0	0	0
7	1.5	64	30	2.09	35	2.5	489	211	56	0	0	0

improved technique of preparation by recirculating the predissolved reagent solution through steel wool as described previously. Flowrates were maintained by a peristaltic pump.

Extra caution was taken to minimize the oxidation of the ferrous ions in the solution to the ferric state. The solutions were prepared with deionized water pre-purged by nitrogen over an extended period (the dissolved oxygen level was detected to be less than 0.6 ppm). Water seals were maintained wherever required, and samples were taken in syringes equipped with louver locks, to avoid any contact with open air. Despite the care taken, there were still appreciable levels of Fe^{3+} detected in the feed solutions (Table 2). Experiments were therefore all conducted in duplicates.

3.0 EXPERIMENTAL RESULTS

Detailed experimental results, analytical data, and experimental breakthrough curves are given in the Appendix. The IX operating capacities determined from the experimental results are summarized in Table 3, and are compared to the exchange capacities calculated from manufacturer's resin capacity data.

The IX operating capacities were determined from the number of equivalents of the respective anion and cation species removed by the known quantity of resin used for the experiment until breakthrough. The breakthrough point was arbitrarily defined as 2% of the feed concentration (for any one of the ionic species).

4.0 COMPUTER SIMULATION RESULTS

In addition to the experimental data, computer simulation results were obtained from the CANDMAN program/1/. The actual experimental conditions such as the feed solution compositions, pH and temperature of three selected runs (Runs 3, 5 and 6), and the design conditions shown in Table 1 were input into the computer program. The predicted equilibrium distribution of the complex ions formed by the reagent anions and metal cations in the solutions, is presented in Table 4.

5.0 DISCUSSION

As shown in Table 3, the experimentally determined capacities were larger than those computed from the manufacturer's resin capacity data by a factor ranging from 1.3 to 2.2 for the cation resin (at different concentrations), and 1.2 to 2.0 for the anion resin. These factors (or capacity ratios) clearly demonstrate the significant discrepancies in estimating the ion exchange capacities based on experimental data and on literature value.

It is believed that the organic ligands; EDTA, oxalic and citric acids, form complexes with the metal ions in the solution, producing complex anions and complex cations which have generally lower valences. Consequently, the respective exchange capacity requirements by the solutions would be reduced (provided the complex ions do not "split" during the exchange process and that the distribution of the species is not significantly affected by the changes in the pH of the column internals). The extent of such

TABLE 3

EXPERIMENTAL RESULTS AND IX CAPACITIES

Run No	Feed Condition (ppm) (Total Fe)	Cation Species						Anion Species						
		Experimental Data (meq removed)/(mL Resin)			Exp. IX Capacity (I) (meq/mL)	Literat. Cap. Data (II) (meq/mL)	Capacity Ratio (I/II)	Experimental Data (meq removed)/mL Resin)				Exp. IX Capacity (I) (meq/mL)	Literat. Cap. Data (II) (meq/mL)	Capacity Ratio (I/II)
		Fe^{2+}	Fe^{3+}	Total Fe				EDTA	Oxalic	Citric	Total Anions			
1	190	0.37	0.37	0.74	0.74	0.42	1.8	0.52	0.03	0.24	0.79	0.79	0.68	1.2
2	200	0.49	0.45	0.94	0.94	0.42	2.2	0.62	0.29	0.0	0.91	0.91	0.68	1.3
3	240	0.59	0.35	0.94	0.94	0.42	2.2	0.63	0.17	0.31	1.11	1.11	0.68	1.6
4	101	0.25	0.28	0.53	0.53	0.42	1.3	0.69	0.20	0.38	1.27	1.27	0.68	1.9
5	127	0.32	0.26	0.58	0.58	0.42	1.4	0.65	0.17	0.35	1.17	1.17	0.68	1.7
6	0	-	-	-	-	-	-	0.67	0.18	0.35	1.20	1.20	0.68	1.8
7	0	-	-	-	-	-	-	0.82	0.15	0.40	1.37	1.37	0.68	2.0

TABLE 4

COMPUTER SIMULATION RESULTS*

		RUN 3	RUN 5	RUN 6	DESIGN CONDITIONS
SOLUTION COMPOSITION PPM					
ANION	EDTA	473	437	409	500
	OXALIC	80	70	69	80
	CITRIC	210	207	190	200
CATION	Fe^{2+}	173	83	0	200
	Fe^{3+}	67	44	0	0
ION	pH	3.4	2.8	2.6	3.5
COMPLEX IONS meq/mL	$EDTA.H_4^{o}$	-	2.88×10^{-5}	4.89×10^{-4}	-
	$EDTA.H_3^{-}$	-	5.10×10^{-5}	6.42×10^{-4}	1.39×10^{-6}
	$EDTA.H_2^{2-}$	4.50×10^{-6}	1.34×10^{-4}	1.25×10^{-3}	1.83×10^{-5}
	$(Fe^{2+}\ EDTA)^{2-}$	6.42×10^{-4}	4.57×10^{-4}	-	2.79×10^{-3}
	$(Fe^{2+}\ EDTA.H)^{-}$	8.07×10^{-5}	2.28×10^{-4}	-	2.78×10^{-4}
	$(Fe^{2+}\ EDTA.H_2)^{o}$	2.18×10^{-5}	2.45×10^{-4}	-	5.96×10^{-5}
	$Oxal.H2^{o}$	8.40×10^{-6}	4.01×10^{-5}	5.51×10^{-5}	6.76×10^{-6}
	$Oxal.H^{-}$	5.90×10^{-4}	7.09×10^{-4}	7.21×10^{-4}	5.99×10^{-4}
	$Oxal^{2-}$	1.61×10^{-4}	4.85×10^{-5}	3.64×10^{-5}	2.05×10^{-4}
	$(Fe^{2+}\ Oxal)^{o}$	4.17×10^{-4}	4.75×10^{-5}	-	3.58×10^{-4}
	$(Fe^{2+}\ Oxal2)_2^{-}$	4.22×10^{-6}	-	-	4.63×10^{-6}
	$Cit.H_3^{o}$	6.18×10^{-4}	$1.76 \times 10^{-3}4$	1.85×10^{-3}	4.86×10^{-4}
	$Cit.H2^{-}$	6.51×10^{-4}	4.67×10^{-4}	3.64×10^{-4}	6.45×10^{-4}
	$Cit.H^{2-}$	1.50×10^{-4}	2.69×10^{-5}	1.56×10^{-5}	1.87×10^{-4}
	Cit^{3-}	1.00×10^{-6}	-	-	1.57×10^{-6}
	$(Fe^{2+}Cit_2.H)^{3-}$	-	-	-	0.37×10^{-6}
	$(Fe^{2+}\ Cit.)^{-}$	2.33×10^{-5}	0.40×10^{-6}	-	2.47×10^{-5}
	$(Fe^{2+}\ Cit.H)^{o}$	2.75×10^{-4}	1.87×10^{-5}	-	2.31×10^{-4}
	TOTAL	3.65×10^{-3}	4.26×10^{-3}	5.42×10^{-3}	5.90×10^{-3}
DISTRIBUTION	$EDTA.H_5^{+}$	-	0.36×10^{-6}	8.26×10^{-6}	-
CATION	$(Fe^{2+}\ EDTA.H_2)^{o}$	2.18×10^{-5}	2.45×10^{-4}	-	5.96×10^{-5}
	$(Fe^{2+}\ Oxal)^{o}2$	4.17×10^{-4}	4.75×10^{-5}	-	3.58×10^{-4}
	$(Fe^{2+}\ Cit.H)^{o}$	2.75×10^{-4}	1.87×10^{-5}	-	2.31×10^{-4}
	Fe^{2+}	4.63×10^{-3}	1.75×10^{-3}	-	3.11×10^{-3}
	$(Fe^{3+}\ EDTA.H_2)^{+}$	1.20×10^{-3}	-	-	-
	TOTAL	6.54×10^{-3}	2.06×10^{-3}	8.26×10^{-6}	3.76×10^{-3}

* All species with concentrations less than 1.0×10^{-7} meq/mL are not included.

reductions can be estimated by evaluating the ionic concentrations of the solution (in meq of counter ions/mL solution), under two different conditions. The first assumes the ionic species in the solution to be totally uncomplexed free ions, and the ionic concentrations can be determined from the known molar concentrations and the equivalent weights of the species. In the second case, the ionic concentrations are calculated based on the assumption that the ions in the solution form complex ions with valences and distributions exactly as those predicted by the CANDMAN program in Table 4. The complexes indicated with electroneutrality in Table 4 are assumed to consist of weakly bound cation and anion species which will split in the column. The ratio of the ionic concentration determined in the second case to that from the first case is an indication of the reduction in IX capacity requirements due to complex ion formation. Table 5 lists the computed ionic concentrations and the resulting percent reductions in capacity requirements.

Table 5 also shows estimates of such reductions based on the experimental data. These reductions can be calculated from the experimentally observed values of the ionic concentrations of the solution and the known molar concentrations of the feed solution (assuming totally uncomplexed free ions). The experimental value of ionic concentration (meq/mL solution) was obtained by dividing the total milliequivalents of column capacity (manufacturer's nominal operating capacity x resin volume in column) by the volume of solution processed up to the breakthrough point.

The experimentally determined percent reduction figures in Table 5 agreed qualitatively with the theoretically predicted values (based on computer simulated complex ion distribution).

Quantitatively, however, only Run 6 showed good agreement, where the experimental data showed a percent reduction in ionic concentration, or IX capacity requirement, of 40.9% for the anions in the solution and the computer simulation results yielded a value of 46.5%. It should be pointed out that in Run 6 the feed solution contained no metal cations, but the partially dissociated reagent anions predicted by the computer model included the protonated species $EDTA.H_5^+$ (see Table 4), which would occupy cation exchange sites. When the solution contained other cationic species, eg. the ferrous and ferric ions in Runs 3 and 5, the discrepancies between the experimentally determined ionic reductions and the theoretically predicted reductions became more profound. Despite such discrepancies, the qualitative interpretations based on the computer simulation results of the CANDMAN program are encouraging. Also, in a separate study/2/, it was observed that the cobalt cations in a cobalt chloride and LND 101A reagent mixture were retained on anion exchange resin; demonstrating the possible presence of negatively charged metal complexes.

The discrepancies are probably also attributable to experimental inaccuracies as well as to the possibly inflated values of ferric ion concentrations reported in the analytical data. It is possible that oxidation of ferrous to ferric ions occurred mostly during sampling and sample analysis. The level of ferric ions actually present during ion exchange might have been much lower. One possible effect of an erroneous ferric ion measurement can be seen by comparing the simulation results in Table 5 for Run 3 and for the design

TABLE 5 - REDUCTION IN IONIC CONCENTRATIONS IN CAN-DECON SOLUTION

Run No	FEED COMPOSITION						CATIONIC CONCENTRATION*					ANIONIC CONCENTRATION*				
							Free Ions	As Complex Ions From Simulation		Experimental Determination		As Free Ions	As Complex Ions From Simulation		Experimental Determination	
	pH	Fe^{2+}	Fe^{3+}	EDTA	OXALIC	CITRIC	(meq/mL) (I)	(meq/mL) (II)	% Reduction (1-II/I)x100	(meq/mL) (III)	% Reduction (1-III/I)x100	(meq/mL) (I)	(meq/mL) (II)	% Reduction (1- II/I)x100	(meq/mL) (III)	% Reduction 1-(III/I)x100
	(ppm)															
3	3.4	173	67	473	80	210	0.0098	0.0065	33.3	0.0044	55.1	0.0115	0.0037	68.4	0.0075	36.3
5	2.8	83	44	437	70	207	0.0053	0.0021	61.4	0.0039	27.0	0.0108	0.0043	60.5	0.0065	40.0
6	2.6	0	0	409	69	190	-	-	-	-	-	0.0101	0.0054	46.5	0.0060	40.9
(Design Conditions)	3.5	200	0	500	80	200	0.0072	0.0034	52.8	-	-	0.0117	0.0059	49.8	-	-

* Ionic concentrations are expressed in terms of (meq of ions)/(mL of solution)

conditions. Although the two solutions contained the same level of total iron of 200 ppm, the presence of the ferric ions in Run 3 resulted in a higher reduction in ionic concentration (68.4% for Run 3 vs. 49.8% for the design conditions). This tends to suggest that the reductions in ionic concentrations predicted from the simulation results shown in Table 5 are probably exaggerated owing to the inflated levels of ferric ion concentrations used in the calculation. However, more in-depth studies are required before definite conclusions can be made.

Based on the experimental data and the theoretical guidance from the computer simulation results, a conservative estimate of the operating capacity of the mixed-bed column can be obtained as follows:

(1) Consider Run 3 and the design conditions of Table 5. Run 3 was selected for consideration because its feed composition approximates the design conditions most closely. Select the ionic reduction factors that will result in the most conservative column capacity estimates under the CAN-DECON conditions. As a result, 33.3% reduction for cations and 36.3% reduction for anions are chosen (from Table 5).

(2) Based on the percent reduction factors selected above, calculate the reduced ionic concentrations for the cations, and anions of the feed solution at design conditions (ie. 500 ppm EDTA, 80 ppm oxalic acid, 200 ppm citric acid and 200 ppm Fe^{2+}).

(3) Calculate the volume of CAN-DECON solution (at the reduced ionic concentration) that can be processed by the column based on manufacturer's resin data. Allow an 80% operating efficiency to account for the fact that manufacturer's resin data indicate only the maximum equilibrium capacity, and operating capacity under dynamic conditions is expected to be less. Two volumes can be calculated based on separate considerations for cationic species and anionic species. Select the lesser of the two values as the limiting quantity.

(4) Or alternatively, determine the column capacity required for treating the design volume of 300 m^3, and calculate the amount of ferrous oxalate that can be removed by the remaining residual capacity.

The estimates for the Bruce CAN-DECON are: the cation exchange capacity of the column is found to be the limiting factor, and a volume of 410 m^3 of the feed (CAN-DECON) solution at the design concentrations can be processed. Or alternatively, the design volume of 300 m^3 can be processed and the residual capacity of the column should be capable of removing an additional amount (40 kg) of ferrous oxalate (which will precipitate as a result of adding oxalic acid to the system, and will function as a corrosion inhibitor. The corresponding amount of $C_2H_2O_4.2H_2O$ is 35 kg). This additional removal would be limited by the residual cation exchange capacity.

6.0 CONCLUSIONS AND RECOMMENDATIONS

1. The operating capacity of the Bruce mixed-bed ion exchange column containing 160 ft^3 of Amberlite IRN 150 and 50 ft^3 of IRN 78 resins

should be adequate for the designed service of Bruce CAN-DECON. Allowing an 80% operating efficiency factor, the designed mixed-bed column should be capable of processing 410 m^3 of feed solution, which is in excess of the design volume of 300 m^3.

2. Alternatively, the column can be utilized to process 300 m^3 of CAN-DECON solution, and the residual column capacity would be sufficient for removing up to 40 kg (limited by residual cation capacity) of ferrous oxalate precipitate formed in the system as a corrosion inhibitor by the addition of extra amounts of oxalic acid (up to 35 kg of $C_2H_2O_4 \cdot 2H_2O$).

3. Owing to the formation of complex ions, design calculations for ion exchange columns in CAN-DECON services cannot be based on manufacturer's resin capacity data. Until more rigorous theoretical guidance can be formulated, only the operating capacities determined experimentally for the specific design conditions and resin(s) are reliable for engineering calculations.

4. The complex ion distribution predicted by the CANDMAN program/1/ cannot be directly applied to predict the conditions inside the IX column, owing to the local pH changes and the shift of equilibrium caused by the removal of ionic species (either as complex ions or "split" ions) by the exchanger. Nevertheless, the reduction in ionic concentration calculated from the computer simulation results can serve as a useful adjunct to the experimental determinations.

5. Further in-depth study is recommended for improving the understanding of: the mechanism of ion exchange in the mixed-bed operation, the effects of the distribution of complex ions on the IX operating capacity, and the effects of the chemical and physical parameters (eg. solution composition, pH, temperature) on the complex ions formation. With improved understanding, more accurate assessments of the process requirements can be established, and overly conservative estimates can be avoided.

ACKNOWLEDGMENT

Dr. G.F. Thomas of Process Chemistry Section provided the computer simulation results generated from the CANDMAN program.

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REFERENCE

1. Thomas, G.F. and A. Husain, "The modelling of Chemical Equilibrium in CAN-DECON Solutions," Ontario Hydro Research Division Report 86-353-K, Toronto, (to be released).

2. Chang, F.H., "Experimental Study of EDTA/IX Interaction," Ontario Hydro Research Division Report, Toronto (in preparation).

APPENDIX

EFFLUENT BREAKTHROUGH CURVES

AND

DETAILED EXPERIMENTAL RESULTS

FIG. 1 — Run 1 Effluent Concentrations

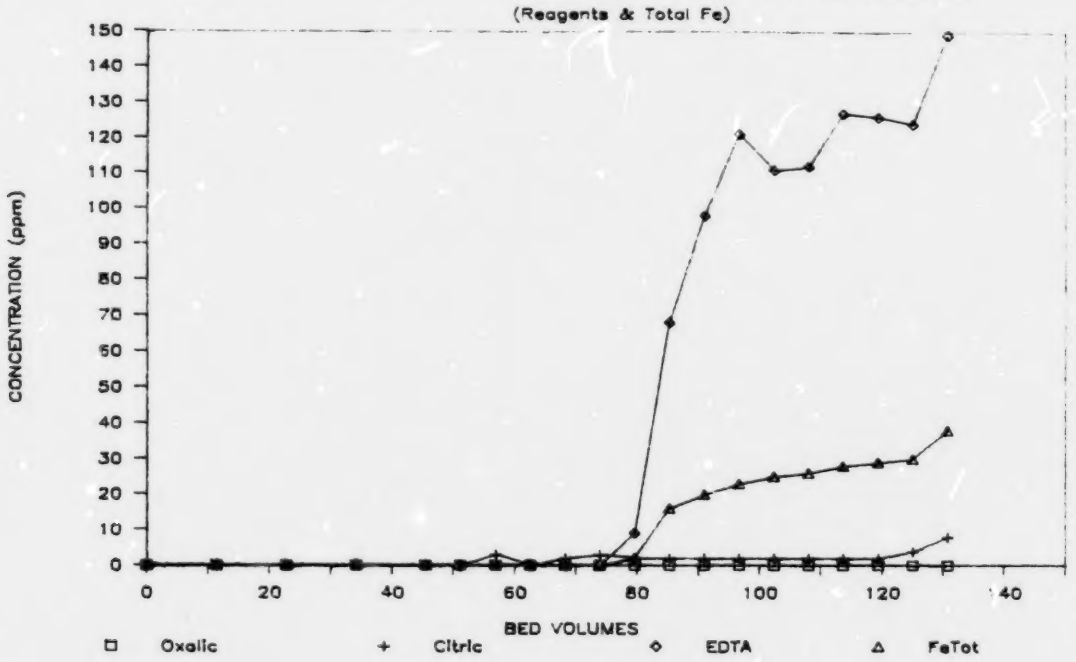


FIG. 2 — Run 2 Effluent Concentrations

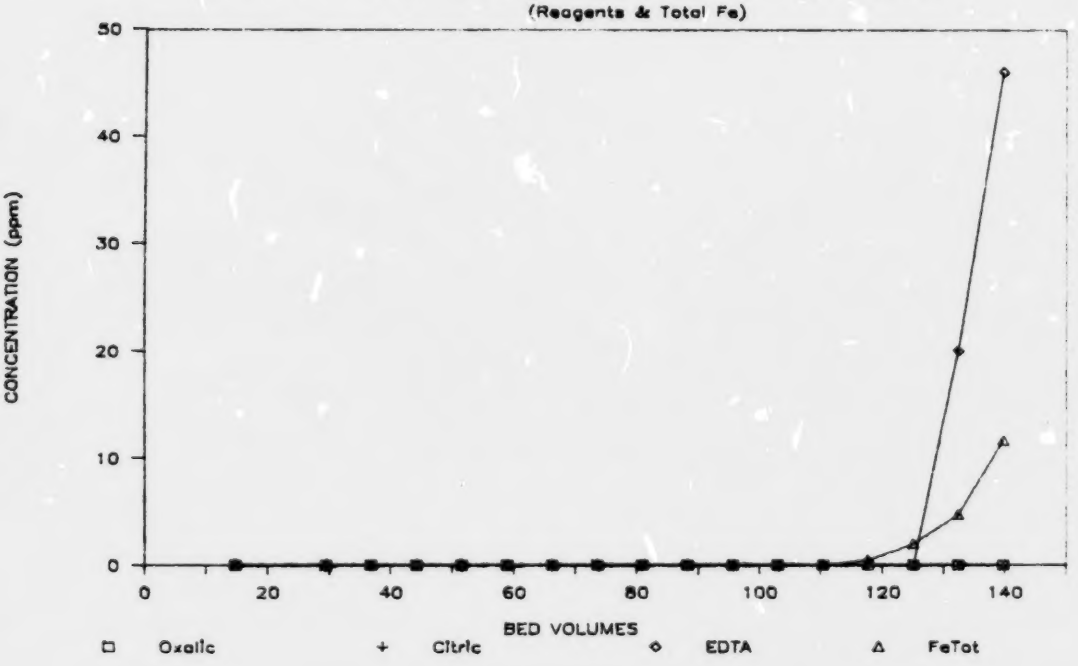


FIG. 3 -- Run 3 Effluent Concentrations

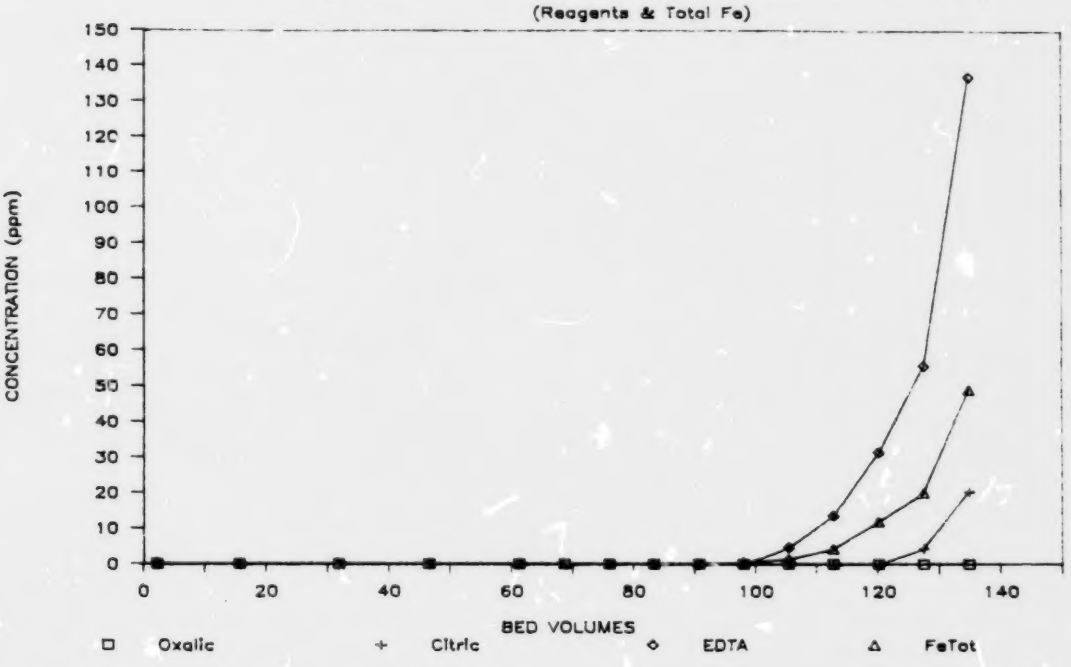


FIG. 4 — Run 4 Effluent Concentrations

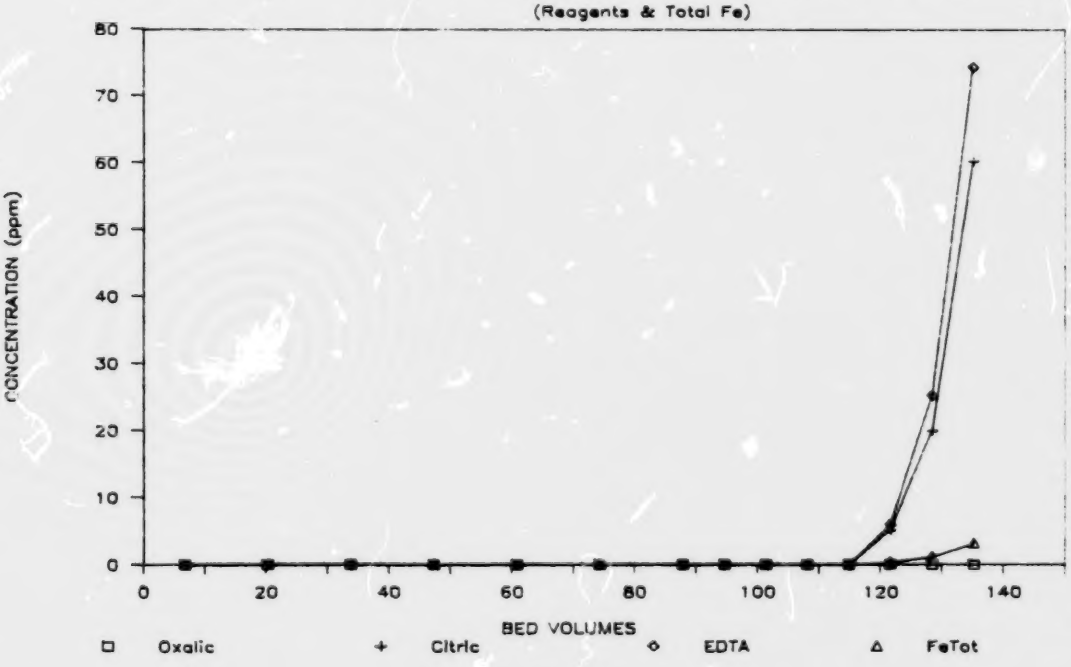


FIG. 5 — Run 5 Effluent Concentrations

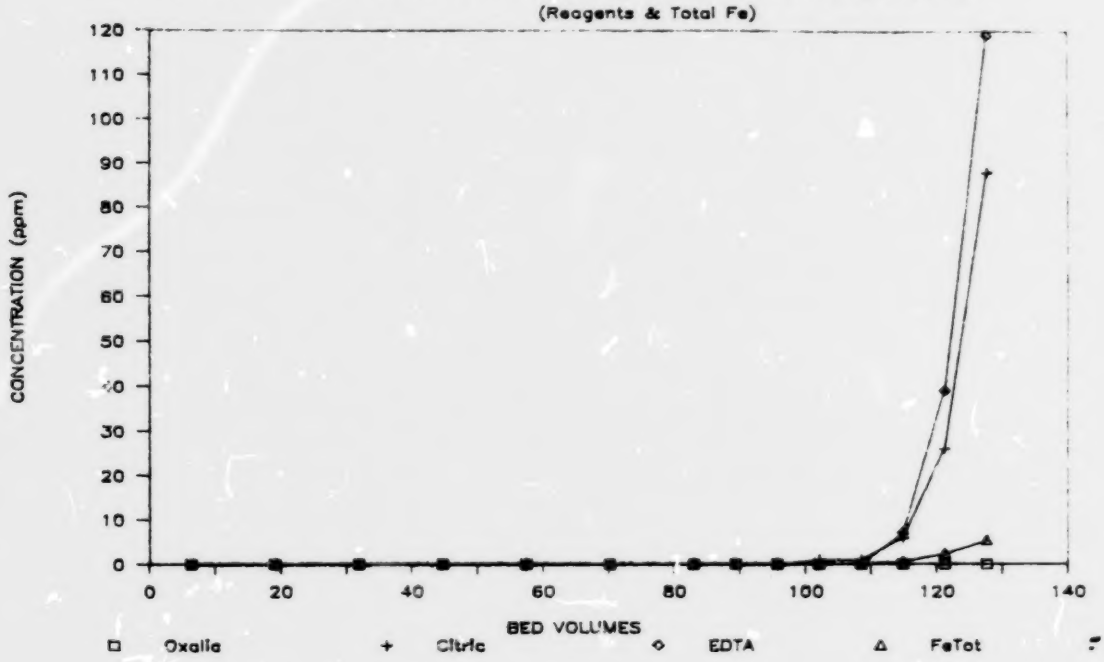


FIG. 6 — Run 6 Effluent Concentrations

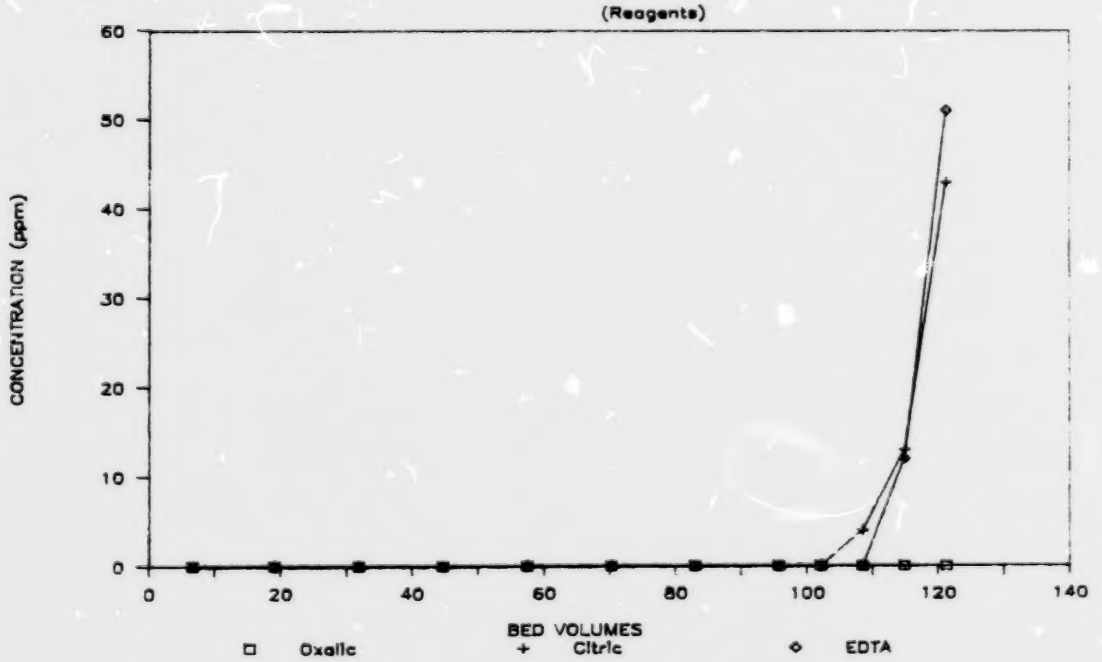
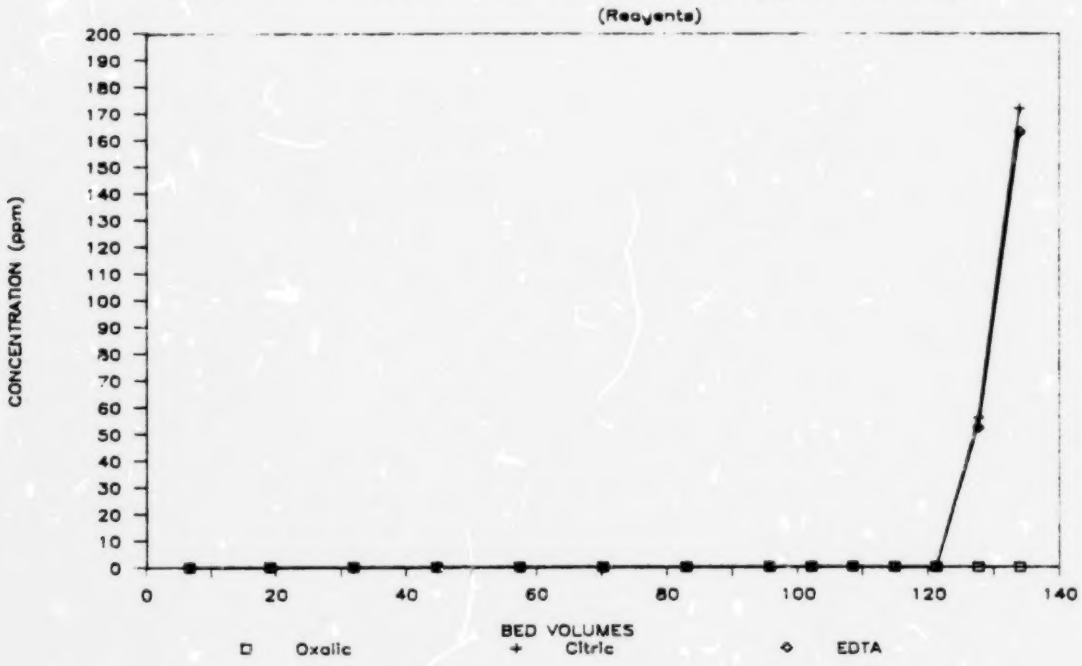


FIG. 7 – Run 7 Effluent Concentrations



Run 1 MIXED-BED ION EXCHANGE CAPACITY DETERMINATION
Column Diameter = 1 inch (2.54 cm) Volume of Resin =690 mL
Feed: pH=3.91 Conductivity=249-340 uS/cm
Total volume passed = 98 L Total time = 375 minutes

Time Hour.Min	Sample #	Oxalic (ppm)	Citric (ppm)	EDTA (ppm)	Fe 2+ (ppm)	Fe 3+ (ppm)	Fe Tot (ppm)	Elapsed T (min)	Bed Vol (B V)
9.00	1F	0.00	150.00	402.00	141.00	89.00	230.00	0.00	
	5F	15.00	166.00	440.00	147.00	83.00	230.00	0.00	
	13F	16.00	163.00	400.00	98.60	71.40	170.00	0.00	
	19F	19.00	173.00	417.00	94.90	75.10	170.00	0.00	
9.30	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10.00	2	0.00	0.00	0.00	0.00	0.00	0.00	30.00	11.36
10.30	3	0.00	0.00	0.00	0.00	0.00	0.00	60.00	22.72
11.00	4	0.00	0.00	0.00	0.00	0.00	0.00	90.00	34.09
11.30	5	0.00	0.00	0.00	0.00	0.00	0.00	120.00	45.45
11.45	6	0.00	0.00	0.00	0.00	0.00	0.00	135.00	51.13
12.00	7	0.00	3.00	0.00	0.00	0.00	0.00	150.00	56.81
12.15	8	0.00	0.00	0.00	0.00	0.00	0.00	165.00	62.49
12.30	9	0.00	2.00	0.00	0.00	0.00	0.00	180.00	68.17
12.45	10	0.00	3.00	0.00	0.00	0.00	0.00	195.00	73.86
13.00	11	0.00	2.00	9.00	0.70	1.30	2.00	210.00	79.54
13.15	12	0.00	2.00	68.00	1.20	14.80	16.00	225.00	85.22
13.30	13	0.00	2.00	98.00	1.40	18.60	20.00	240.00	90.90
13.45	14	0.00	2.00	121.00	1.50	21.50	23.00	255.00	96.58
14.00	15	0.00	2.00	111.00	1.70	23.30	25.00	270.00	102.26
14.15	16	0.00	2.00	112.00	2.12	23.88	26.00	285.00	107.94
14.30	17	0.00	2.00	127.00	2.40	25.60	28.00	300.00	113.62
14.45	18	0.00	2.00	126.00	3.00	26.00	29.00	315.00	119.30
15.00	19	0.00	4.00	124.00	4.00	26.00	30.00	330.00	124.99
15.15	20	0.00	8.00	149.00	5.70	32.30	38.00	345.00	130.67

Run 2 MIXED-BED ION EXCHANGE CAPACITY DETERMINATION
Column Diameter = 1.5 cm Volume of Resin = 64 mL
Feed: pH=3.3 Conductivity=
Total vol passed = 8 L Time = 255 min

Time Hour.Min	Sample #	Oxalic (ppm)	Citric (ppm)	EDTA (ppm)	Fe 2+ (ppm)	Fe 3+ (ppm)	Fe Tot (ppm)	Elapsed T (min)	Bed Vol (B V)
11.00	1F	0.00	174.00	394.00	128.00	72.00	200.00	0.00	
	12F	0.00	157.00	415.00	135.00	65.00	200.00	0.00	
	16F	0.00	177.00	412.00	109.00	91.00	200.00	0.00	
11.30	1	0.00	0.00	0.00	0.00	0.00	0.00	30.00	14.71
12.00	2	0.00	0.00	0.00	0.00	0.00	0.00	60.00	29.41
12.15	3	0.00	0.00	0.00	0.00	0.00	0.00	75.00	36.76
12.30	4	0.00	0.00	0.00	0.00	0.00	0.00	90.00	44.12
12.45	5	0.00	0.00	0.00	0.00	0.00	0.00	105.00	51.47
13.00	6	0.00	0.00	0.00	0.00	0.00	0.00	120.00	58.82
13.15	7	0.00	0.00	0.00	0.00	0.00	0.00	135.00	66.18
13.30	8	0.00	0.00	0.00	0.00	0.00	0.00	150.00	73.53
13.45	9	0.00	0.00	0.00	0.00	0.00	0.00	165.00	80.88
14.00	10	0.00	0.00	0.00	0.00	0.00	0.00	180.00	88.24
14.15	11	0.00	0.00	0.00	0.00	0.00	0.00	195.00	95.59
14.30	12	0.00	0.00	0.00	0.00	0.00	0.00	210.00	102.94
14.45	13	0.00	0.00	0.00	0.00	0.00	0.00	225.00	110.29
15.00	14	0.00	0.00	0.00	0.00	0.50	0.50	240.00	117.65
15.15	15	0.00	0.00	0.00	0.00	2.00	2.00	255.00	125.00
15.30	16	0.00	0.00	20.00	0.50	4.20	4.70	270.00	132.35
15.45	17	0.00	0.00	46.00	1.50	10.10	11.60	285.00	139.71

Run 3 MIXED-BED ION EXCHANGE CAPACITY DETERMINATION
Column Diameter = 1.5 cm Volume of Resin = 64 mL
Feed: pH=3.41 Conductivity=
Total vol passed = 7.85 L Time = 275 min

Time Hour.Min	Sample #	Oxalic (ppm)	Citric (ppm)	EDTA (ppm)	Fe 2+ (ppm)	Fe 3+ (ppm)	Fe Tot (ppm)	Elapsed T (min)	Bed Vol (B V)
18.55	1F	55.70	235.00	543.00	165.00	50.00	215.00	0.00	
	5F	76.00	208.00	474.00	187.00	53.00	240.00	0.00	
	9F	81.10	210.00	492.00	144.00	96.00	240.00	0.00	
	13F	81.00	211.00	452.00	189.00	51.00	240.00		
19.00	1	0.00	0.00	0.00	0.00	0.00	0.00	5.00	2.23
19.30	2	0.00	0.00	0.00	0.00	0.00	0.00	35.00	15.61
20.00	3	0.00	0.00	0.00	0.00	0.00	0.00	65.00	31.86
20.30	4	0.00	0.00	0.00	0.00	0.00	0.00	95.00	46.57
21.00	5	0.00	0.00	0.00	0.00	0.00	0.00	125.00	61.27
21.15	6	0.00	0.00	0.00	0.00	0.00	0.00	140.00	68.63
21.30	7	0.00	0.00	0.00	0.00	0.00	0.00	155.00	75.98
21.45	8	0.00	0.00	0.00	0.00	0.00	0.00	170.00	83.33
22.00	9	0.00	0.00	0.00	0.00	0.20	0.20	185.00	90.69
22.15	10	0.00	0.00	0.00	0.00	0.50	0.50	200.00	98.04
22.30	11	0.00	0.00	4.60	0.90	0.60	1.50	215.00	105.39
22.45	12	0.00	0.00	13.60	2.70	0.00	4.30	230.00	112.75
23.00	13	0.00	0.00	31.40	6.40	5.60	12.00	245.00	120.10
23.15	14	0.00	4.50	55.60	9.40	10.60	20.00	260.00	127.45
23.30	15	0.00	20.50	137.00	22.80	26.20	49.00	275.00	134.80

Run 4 MIXED-BED ION EXCHANGE CAPACITY DETERMINATION
Column Diameter = 1.5 cm Volume of Resin = 64 mL
Feed: pH=2.55 Conductivity= 1001 uS/cm
Total vol passed = 8.65 L Time = 300 min

Time Hour.Min	Sample #	Oxalic (ppm)	Citric (ppm)	EDTA (ppm)	Fe 2+ (ppm)	Fe 3+ (ppm)	Fe Tot (ppm)	Elapsed T (min)	Bed Vol (B V)
13.15	1F	68.50	192.10	407.30	50.50	46.50	97.00	0.00	
	5F	75.00	197.40	412.80	58.20	41.80	100.00	0.00	
	11F	77.70	202.50	418.30	64.50	40.50	105.00	0.00	
13.30	1	0.00	0.00	0.00	0.00	0.00	0.00	15.00	6.76
14.00	2	0.00	0.00	0.00	0.00	0.00	0.00	45.00	20.27
14.30	3	0.00	0.00	0.00	0.00	0.00	0.00	75.00	33.79
15.00	4	0.00	0.00	0.00	0.00	0.00	0.00	105.00	47.30
15.30	5	0.00	0.00	0.00	0.00	0.00	0.00	135.00	60.82
16.00	6	0.00	0.00	0.00	0.00	0.00	0.00	165.00	74.34
16.30	7	0.00	0.00	0.00	0.00	0.00	0.00	195.00	87.85
16.45	8	0.00	0.00	0.00	0.00	0.60	0.00	210.00	94.61
17.00	9	0.00	0.00	0.00	0.00	0.00	0.00	225.00	101.37
17.15	10	0.00	0.00	0.00	0.00	0.00	0.00	240.00	108.12
17.30	11	0.00	0.00	0.00	0.00	0.00	0.00	255.00	114.88
17.45	12	0.00	5.20	6.00	0.00	0.40	0.40	270.00	121.64
18.00	13	0.00	20.00	25.20	0.00	1.20	1.20	285.00	128.40
18.15	14	0.00	60.30	74.30	0.00	3.20	3.20	300.00	135.16

Run 5 MIXED-BED ION EXCHANGE CAPACITY DETERMINATION
Column Diameter = 1.5 cm Volume of Resin = 64 mL
Feed: pH=2.75 Conductivity= 886 uS/cm
Total vol passed = 9.8 L Time = 360 min

Time Hour.Min	Sample #	Oxalic (ppm)	Citric (ppm)	EDTA (ppm)	Fe 2+ (ppm)	Fe 3+ (ppm)	Fe Tot (ppm)	Elapsed T (min)	Bed Vol (B V)
13.45	1F	74.00	212.00	452.00	75.90	51.10	127.00	0.00	
	5F	66.00	205.00	416.00	84.00	43.00	127.00	0.00	
	11F	75.00	205.00	433.00	81.30	45.70	127.00	0.00	
	18F	66.00	207.00	446.00	91.90	35.10	127.00		
14.00	1	0.00	0.00	0.00	0.00	0.00	0.00	15.00	6.38
14.30	2	0.00	0.00	0.00	0.00	0.00	0.00	45.00	19.14
15.00	3	0.00	0.00	0.00	0.00	0.00	0.00	75.00	31.90
15.30	4	0.00	0.00	0.00	0.00	0.00	0.00	105.00	44.66
16.00	5	0.00	0.00	0.00	0.00	0.00	0.00	135.00	57.42
16.30	6	0.00	0.00	0.00	0.00	0.00	0.00	165.00	70.18
17.00	7	0.00	0.00	0.00	0.00	0.00	0.00	195.00	82.94
17.15	8	0.00	0.00	0.00	0.00	0.00	0.00	210.00	89.32
17.30	9	0.00	0.00	0.00	0.00	0.00	0.00	225.00	95.70
17.45	10	0.00	1.00	0.00	0.00	0.00	0.00	240.00	102.08
18.00	11	0.00	1.00	0.00	0.00	0.24	0.24	255.00	108.46
18.15	12	0.00	6.00	7.00	0.00	0.66	0.66	270.00	114.84
18.30	13	0.00	26.00	39.00	0.00	2.40	2.40	285.00	121.22
18.45	14	0.00	88.00	119.00	0.00	5.40	5.40	300.00	127.60
19.00	15	0.00	157.00	212.00	0.00	7.50	7.50	315.00	133.98
19.15	16	0.00	298.00	404.00	0.00	6.10	6.10	330.00	140.36
19.30	17							345.00	146.74
19.45	18	0.00	268.00	481.00	0.00	5.70	5.70	360.00	153.13

Run 6 MIXED-BED ION EXCHANGE CAPACITY DETERMINATION
Column Diameter = 1.5 cm Volume of Resin = 64 mL
Feed: pH=2.65 Conductivity= 1076 uS/cm
Total vol passed = 8.8 L Time = 315 min

Time Hour.Min	Sample #	Oxalic (ppm)	Citric (ppm)	EDTA (ppm)	Fe 2+ (ppm)	Fe 3+ (ppm)	Fe Tot (ppm)	Elapsed T (min)	Bed Vol (B V)
9.30	1F	75.00	197.00	427.00	0.00	0.00	0.00	0.00	
	5F	69.00	185.00	392.00	0.00	0.00	0.00	0.00	
	11F	64.00	188.00	410.00	0.00	0.00	0.00	0.00	
9.45	1	0.00	0.00	0.00	0.00	0.00	0.00	15.00	6.38
10.15	2	0.00	0.00	0.00	0.00	0.00	0.00	45.00	19.14
10.45	3	0.00	0.00	0.00	0.00	0.00	0.00	75.00	31.90
11.15	4	0.00	0.00	0.00	0.00	0.00	0.00	105.00	44.66
11.45	5	0.00	0.00	0.00	0.00	0.00	0.00	135.00	57.42
12.15	6	0.00	0.00	0.00	0.00	0.00	0.00	165.00	70.18
12.45	7	0.00	0.00	0.00	0.00	0.00	0.00	195.00	82.94
13.15	8	0.00	0.00	0.00	0.00	0.00	0.00	225.00	95.70
13.30	9	0.00	0.00	0.00	0.00	0.00	0.00	240.00	102.08
13.45	10	0.00	4.00	0.00	0.00	0.00	0.00	255.00	108.46
14.00	11	0.00	13.00	12.00	0.00	0.00	0.00	270.00	114.84
14.15	12	0.00	43.00	51.00	0.00	0.00	0.00	285.00	121.22
14.30	13	0.00	135.00	165.00	0.00	0.00	0.00	300.00	127.60
14.45	14	0.00	271.00	356.00	0.00	0.00	0.00	315.00	133.98

Run 7 MIXED-BED ION EXCHANGE CAPACITY DETERMINATION
Column Diameter = 1.5 cm Volume of Resin = 64 mL
Feed: pH=2.51 Conductivity= 1112 uS/cm
Total vol passed = 9.6 L Time = 315 min

Time Hour.Min	Sample #	Oxalic (ppm)	Citric (ppm)	EDTA (ppm)	Fe 2+ (ppm)	Fe 3+ (ppm)	Fe Tot (ppm)	Elapsed T (min)	Bed Vol (B V)
13.45	1F	56.00	225.00	512.00	0.00	0.00	0.00	0.00	
	5F	54.00	217.00	502.00	0.00	0.00	0.00	0.00	
	11F	53.00	198.00	466.00	0.00	0.00	0.00	0.00	
	16F	63.00	205.00	476.00	0.00	0.00	0.00		
14.00	1	0.00	0.00	0.00	0.00	0.00	0.00	15.00	6.55
14.30	2	0.00	0.00	0.00	0.00	0.00	0.00	45.00	19.14
15.00	3	0.00	0.00	0.00	0.00	0.00	0.00	75.00	31.90
15.30	4	0.00	0.00	0.00	0.00	0.00	0.00	105.00	44.66
16.00	5	0.00	0.00	0.00	0.00	0.00	0.00	135.00	57.42
16.30	6	0.00	0.00	0.00	0.00	0.00	0.00	165.00	70.18
17.00	7	0.00	0.00	0.00	0.00	0.00	0.00	195.00	82.94
17.30	8	0.00	0.00	0.00	0.00	0.00	0.00	225.00	95.70
17.45	9	0.00	0.00	0.00	0.00	0.00	0.00	240.00	102.08
18.00	10	0.00	0.00	0.00	0.00	0.00	0.00	255.00	108.46
18.15	11	0.00	0.00	0.00	0.00	0.00	0.00	270.00	114.84
18.30	12	0.00	0.00	0.00	0.00	0.00	0.00	285.00	121.22
18.45	13	0.00	56.00	52.00	0.00	0.00	0.00	300.00	127.60
19.00	14	0.00	172.00	163.00	0.00	0.00	0.00	315.00	133.98
19.15	15	0.00	275.00	319.00	0.00	0.00	0.00	330.00	140.36
19.30	16	0.00	309.00	449.00	0.00	0.00	0.00	345.00	146.74

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